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PERFORMANCE OF DESICCANTS IN THE DRY PAN TEST FOR WATER VAPOR PERMEANCE OF MEMBRANES[1]

BY S. C. CHANG[2] AND N. B. HUTCHEON[3]

ABSTRACT

Tests were carried out to establish the magnitude of the variations attributable to desiccant condition in the dry pan test for water vapor permeance of membranes. The change in slope of the curve of weight gain vs. time for the dry pan test was used to predict the apparent relative humidity on the desiccant side of the membrane for various amounts of moisture gain for three different desiccants at three different rates of moisture transmission. The relative humidities found under the dynamic conditions of test were all much higher than the corresponding equilibrium data quoted for desiccants, and were shown to be influenced by type and initial dryness of desiccant and by the degree of agitation during test. The test procedure used would appear to have some value also in the assessment of solid sorbents for use in certain practical drying applications.

INTRODUCTION

It was found, during studies being carried out on the influence of various factors on the transmission of water vapor through sheet materials, that the kind and condition of the desiccant used had a marked bearing on the results. Tests were carried out to establish the order of magnitude of the variations to be expected from this source, and to indicate if possible which of the commonly used desiccants were the most suitable.

Packaging membranes of various kinds are commonly selected for their ability to control the movement of water vapor through them. This presupposes the ability to determine by some accepted standard means the relative permeabilities of the available materials. A somewhat similar situation arises in the case of the design of the enclosing structure of buildings where it is now standard practice to incorporate one or more membranes as vapor barriers in a wall, floor, or ceiling. Other materials may be required to transmit water vapor and so must be tested for their compliance with some minimum standard.

At present, the interest in water vapor transmission ratings arises most frequently in the case of relatively thin membrane materials such as foils, plastic films, treated papers and boards, and paint films. Several test methods

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Contribution from the Department of Mechanical Engineering, University of Saskatchewan, Saskatoon, Sask.
[2] *Research assistant, Mechanical Engineering Department, University of Saskatchewan.*
[3] *Professor of Mechanical Engineering, University of Saskatchewan.*

are available for determining water vapor transmission through such membranes, depending on the use for which they are being assessed. They all provide for establishment of vapor flow under standardized conditions of temperature, vapor pressure, and vapor pressure difference and for measurement of the rate of flow. Simplicity is achieved by testing under isothermal conditions at one arbitrarily fixed temperature with arbitrarily selected relative humidities, and therefore vapor pressures, maintained on either side of the test membrane, although it is well known that variations in all three of these factors may markedly affect the result obtained. A further simplification is achieved by accepting for the test purposes the vapor pressure over a desiccant, or alternatively the vapor pressure over pure water, as the vapor pressure on one side of the test sample. It then becomes possible to seal the test sample as a cover over a pan containing either a desiccant or pure water and to establish the rate of water vapor transmission by weighing the pan at suitable intervals of exposure to a conditioned atmosphere.

The TAPPI method T-448m-49 employing a desiccant, commonly referred to as a dry pan method, is widely known and used in Canada. This method is identical to ASTM F-998-48T, Tentative Method of Test for Water Vapour Permeance of Paper Board and other Sheet Materials. It has recently been adopted as the method of test for water vapor transmission through building papers covered by specifications 9-GP-2 and 9-GP-3 of the Canadian Government Specifications Board. Water vapor permeability is defined for this method as the weight of water transmitted per unit of time, per unit area, measured while the specimen separates an atmosphere below 5% relative humidity on one face from the standard atmosphere of 50% R.H. and 73°F. on the other face. A sample test area of not less than 50 sq. cm. is recommended. The pan is tested in the inverted or paper down position with the desiccant retained against the membrane. Anhydrous magnesium perchlorate is recommended as the standard desiccant but anhydrous calcium chloride is also accepted. A second method TAPPI T-464m is available for tests at high humidity and high temperature.

Some investigators, recognizing that the water vapor transmission rate is a function, not only of vapor pressure difference, but of other factors peculiar to a particular method of test, maintain that results should only be quoted as in the TAPPI method, as weight gain through unit area in unit time for the particular test method used. Such results are then of value only for comparison of materials tested in the same way. Others, accepting Fick's Law as a basis for calculating vapor transmission, prefer to have the results of tests expressed as permeances (unit pressure difference) or as permeabilities (unit pressure difference, unit thickness). Babbitt (1) used the term diffusance and expressed results as grams per square meter per 24 hr. per millimeter of mercury vapor pressure difference. Present engineering practice in the United States has adopted the "perm" as the unit of permeance, 1 perm being 1 grain per square foot per hour for a vapor pressure difference of 1 in. of mercury (6).

This unit will probably find general acceptance in Canada also. Test data may therefore be reduced according to the equation

$$[1] \qquad D = \Delta W/[\Delta\theta A(P_1 - P_2)]$$

where D = permeance in perms,
ΔW = weight gain in grains in $\Delta\theta$ hours, through test area A sq. ft., and
P_1, P_2 = the vapor pressures in in. Hg on either side of the specimen.

This same equation, rearranged, may be used to predict the flow of water vapor (1, 6), provided that suitable values of D can be assigned. D is not a true coefficient, but is known to be a function of temperature and vapor pressure, or relative humidity, for most practical materials. Much work remains to be done to provide the appropriate values of D for any given material, and for particular sets of conditions. Re-examination of the standard test procedures for permeance measurement provides a good starting point, leading to a better understanding not only of the meaning and value of the results of these tests but of the main phenomenon involved as well.

The equation given above for reduction of dry pan test data assumes that proper values can be assigned to P_1 and P_2. Evaluation of P_1 presents no more than the usual difficulty of measuring vapor pressure in a room or cabinet. P_2, over the desiccant, is commonly assumed to be zero. Some authorities recommend that a pressure corresponding to 5% relative humidity be assumed over the desiccant, particularly when calcium chloride is used. The definition of permeability in the TAPPI method implies that the humidity may vary from 0% to 5%, producing a possible variation of 10% in the test results from this source alone. If P_2 varies during the test, as the desiccant gains in moisture content, it is clear that the rate of moisture gain, $\Delta W/\Delta\theta$, will also vary, and that appropriate, corresponding values of P_2 and $\Delta W/\Delta\theta$ must be used in establishing D accurately.

It is known that the increase or decrease of the weight of water held by a substance is dependent upon the partial vapor pressure of the held water in relation to the vapor pressure of the surrounding atmosphere. Those substances which can retain water at very low vapor pressure even when the water content is relatively high are known as desiccants. They have the property of sorbing water vapor brought into contact with them and consequently they are able to lower the vapor pressure inside a closed space where the supply of water vapor is limited, as in the case of the dry pan test.

Ideally, the vapor pressure of the water held by a desiccant should be measurable by some direct method such as sampling the vapor pressure in an atmosphere in equilibrium with it. However, the vapor pressure of the desiccant is so low in most cases that the usual methods of humidity measurement are inadequate. A search of the literature reveals that few studies of this type have been made. Approximations to equilibrium vapor pressures have been made in most cases by a flow method in which air of known moisture

content is passed through a long tube of desiccant. The final vapor pressure is calculated from the moisture remaining in the air as determined by the difference between initial and sorbed moisture. Results obtained by such methods, taken from the International Critical Tables and other sources, are shown in Table I. It may be noted that these values of relative humidity are generally very low. The relative humidity for the trihydrate of magnesium perchlorate is still very low even though this represents an increase in weight due to water

TABLE I

RESIDUAL WATER AT EQUILIBRIUM OVER VARIOUS DESICCANTS

Desiccant	Residual water at 25°C.		Source of data
	Mgm. per liter	Relative humidity, %	
P_2O_5	2.5×10^{-5}	0.0001	(8)
$Mg(ClO_4)_2$, anhydrous	5×10^{-4}	0.0021	(12)
$Mg(ClO_4)_2 \cdot 3H_2O$ (30% water)	2×10^{-3}	0.0085	(12)
$CaCl_2$, anhydrous	0.14 to 0.25	0.6 to 0.11	(7)
$CaCl_2 \cdot H_2O$ (17% water)		3	(11)
$CaCl_2 \cdot 2H_2O$ (33% water)		4	(11)
$CaCl_2 \cdot 6H_2O$ (98% water)		20	(11)
CaO	3×10^{-3}	0.013	(3)
Silica gel, dry	0.030	0.13	(3)
10% water		7.4	(4)
15% water		20.3	(4)
20% water		32	(4)
H_2SO_4, 95% conc.	3×10^{-3}	0.013	(2)
80% conc.		0.8	(13)
75% conc.		2.3	(13)
70% conc.		5.2	(13)
65% conc.		9.8	(13)

of 30% over the anhydrous form. Calcium chloride is shown to be capable of taking on more than 33% of water before a 5% level of relative humidity is exceeded.

The data of Table I, indicating as they do, that many desiccants can maintain low equilibrium vapor pressures even after substantial moisture gains, are apt to be misleading in terms of the dry pan test. In this test, a flow condition is produced and maintained. Water vapor passing through the membrane must first reach and be sorbed by the desiccant. If an air film of substantial thickness exists over the desiccant, diffusion must take place through it, and as a result a vapor pressure difference necessary to support vapor flow is maintained. Even where no air film exists, diffusion must first take place through the void atmosphere before reaching the desiccant surface. The desiccant layer next the membrane tends to take on the water vapor first, and gradually a gradient condition of both moisture content and of vapor pressure in the void atmosphere is set up through the desiccant bed. As the desiccant is continually taking on water, equilibrium conditions are never reached. The values listed in Table I which may be useful to compare

the relative sorbing efficiencies of different desiccants may bear little relation to the actual vapor pressure, P_2, over the desiccant which must be known for the calculation of permeance from dry pan test data.

The factors which at this point would appear to affect the effective vapor pressure, P_2, at the inner face of the membrane may now be listed:

1. Rate of moisture flow.
2. Kind of desiccant.
3. Thickness of desiccant bed provided.
4. Physical condition of the desiccant, including its moisture content.
5. Permeance of the layer of air or any other material interposed between the desiccant and the membrane under test.
6. Direction of flow, whether up or down, which may influence the transfer of vapor by convection.
7. Extent of the agitation produced in the desiccant either periodically as in handling during weighing, or intentionally by mechanical means during the test.

There would appear to be no satisfactory way of evaluating the combined effect of these factors except by tests for certain specific cases.

There is no simple way to measure the value of P_2 directly, owing to its low magnitude, and especially with the limited space provided inside the test pan. However its approximate value can be obtained indirectly by observing the changes in the rate of the weight increase during a test, provided that it can be assumed that the rate of moisture transfer is directly proportional to the pressure difference across the membrane, and that changes in this rate are primarily due to changes in the effective pressure on the desiccant side. A typical curve of moisture gain plotted against time is shown in Fig. 1. The

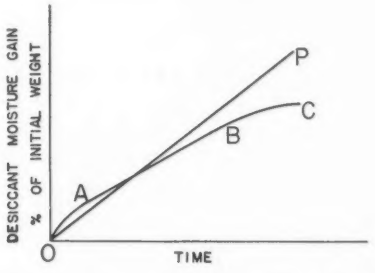

FIG. 1. Desiccant moisture gain, with time, in the dry pan test.

straight line OP indicates the ideal condition where the vapor pressure P_2 is zero throughout the test and hence the rate of the moisture gain is a constant at a maximum value. In the actual case, the rate of moisture gain is not a constant and the curve takes the shape shown by $OABC$. The specimen initially

must adjust its moisture content to the conditions established by the test and this is reflected in the initial part of the curve, OA, which may be either concave to the time axis as shown, or convex, depending on the initial moisture condition of the specimen. AB is the part of the curve usually regarded as a straight line and used for calculation of permeance. However a close investigation will show that AB is not exactly a straight line and that its slope gradually decreases from A to B since the moisture content of the desiccant continuously builds up and is accompanied by an increase in water vapor pressure over the desiccant. The slope further decreases after B and the curve may become horizontal if the test is carried far enough.

Let k be the slope of the straight line OP and q or $dW/d\theta$ be the slope of the curve $OABC$ at any point between A and B. The value of k will always be greater than q owing to the fact that P_2 is actually not zero.

Now if q can be assumed to be proportional to $P_1 - P_2$ at any point, it follows that q will also be proportional to $R_1 - R_2$ where R_1, R_2 are the relative humidites in the cabinet and inside the pan, at the same temperature throughout. It follows also that

$$q/k = (R_1 - R_2)/(R_1 - 0)$$

[2] and $$R_2 = (R_1/k)(k - q)$$

The value of k for a membrane may be determined by testing with a desiccant which is known to maintain a vapor pressure very close to zero. Equation 2 may then be applied, using values of q applicable to various portions of the weight–time curve, to calculate values of R_2. These may then be plotted as in Fig. 2 against the corresponding values of moisture gain of the desiccant. If the condition of the desiccant at the start of the test is known, the ordinates

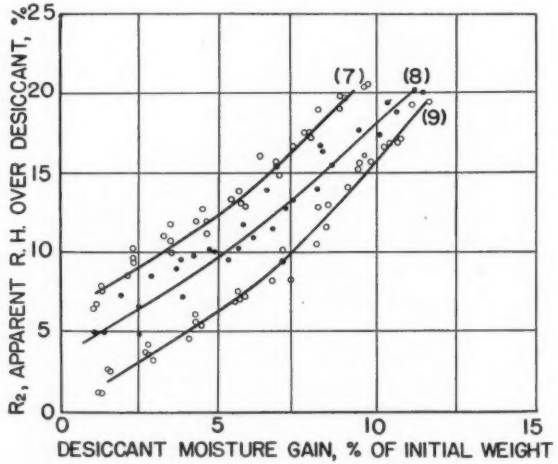

FIG. 2. Apparent relative humidities over silica gel in the dry pan test at various moisture gains. Curves repeated in Fig. 5.

may be corrected to moisture content instead of moisture gain. Three sets of data from actual tests with silica gel as desiccant are presented in Fig. 2.

TEST PROCEDURE

Tests were carried out using three desiccants, with three papers providing a range of permeances from 4.9 to 31 perms. The procedures followed in testing were essentially those of the TAPPI dry pan test. Weight gain vs. time data were obtained and were subsequently analyzed according to the method of the previous section to provide corresponding values of apparent relative humidity and weight gain from which curves were plotted for each combination of variables.

Pans were arranged in three ways for test. Some were tested with the paper up so that an air space of approximately 0.3 in. was left between paper and desiccant. Other pans were tested paper down so that the desiccant was directly in contact with the paper. Still other pans were mounted around the perimeter of a disk which was rotated slowly throughout the test so that the desiccant was tumbled in the pan continuously. The axis of rotation was horizontal and the pans were arranged with their circular cross sections in the plane of rotation.

The design of the pans used was as shown in Fig. 3. The bottoms, which were waxed on, could be removed for replacement of desiccant without

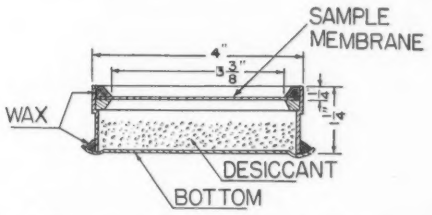

FIG. 3. Test pan used in Series *B* and subsequent tests.

disturbing the test membrane or its seal with the pan. This feature, although of little value in routine testing, is of great use in special investigations. The design shown is now accepted as standard by the Division of Building Research, National Research Council, for vapor permeability testing and was patterned after a design by the National Bureau of Standards.

The desiccants selected for investigation were calcium chloride, silica gel, and magnesium perchlorate. Some difficulty, not at first fully appreciated, was encountered in finding a suitable means of assessing the initial moisture contents and the quality of these materials.

The calcium chloride was of the grade commonly used in chemistry laboratories for general drying use, purchased in 100 lb. steel drums, not reagent grade and not guaranteed as to quality, granular in form. Similar material had previously been extensively used in dry pan tests in the laboratory. After some study it was concluded that the moisture content of the material

as received might best be described in terms of the loss in weight when heated for 24 hr. at 200°C. A number of samples from the single drum from which all the calcium chloride was obtained showed from 7 to 9% loss in weight on heating. The heating treatment was shown to give reproducible results, and samples allowed to gain known amounts of moisture were reduced to the same "dry" weight upon reconditioning.

The silica gel was of the quality supplied for use in refrigerant driers, provided in sealed containers by a chemical supply house. It was found to lose 1½% by weight upon heating for 24 hr. at 200°C.

The magnesium perchlorate used was purchased in 1 lb. and 5 lb. sealed bottles from reliable sources and was supplied as granular, anhydrous, and said to be a high quality desiccant. In view of the high drying power attributed to magnesium perchlorate, not only in the anhydrous form but in the trihydrate form after a 30% increase in moisture content, and of the remoteness of the possibility that it was other than anhydrous as stated, it was decided to accept this desiccant as standard, and to assume that the relative humidity over it, at low moisture gain, was, for practical purposes, zero.

The membranes used for test were three building papers which had already been the subject of considerable study in the laboratory and were believed to be reasonably stable as to permeance. It was not considered that differences other than stability and permeance would be of consequence in the tests. It was found, however, that surface roughness affected in one case the amount of calcium chloride dust held on the back of the paper in the rotated test, and in the case of a fourth paper whose low permeance was due mainly to a surface coating, the tumbling of the desiccant appeared to damage the coating and to produce an increase in permeance.

Paper F4.9 was an asphalt-saturated, 12-lb. felt having a permeance of 4.9 perms. Paper S16 was an asphalt-saturated sheathing paper having a permeance of 16 perms. Paper K31 was a treated kraft sheathing paper having a smooth, lightly waxed surface, and with a permeance of 31 perms.

The experimental work was carried out in two different cabinets. Series *A* tests were performed in a well-controlled, liquid-jacketed cabinet at 77°F. and 52% R.H. The pans of 30 sq. cm. area were supported paper side down from a ring mounted inside the cabinet. They were weighed without being removed from the cabinet, each one being picked up in turn on the end of a long vertical wire running through the top of the cabinet to the analytical balance above. In this way, the pans were not subjected to changes in temperature and humidity during weighing. Relative humidity was controlled and measured to better than ½% R.H. The Series *B* tests were carried out in a larger cabinet with pans of 57.5 sq. cm. area, and conditions maintained at 73.5°F. and 52% R.H. The device for rotating the pans during test was provided in this cabinet, as were racks for supporting the pans in either the paper up or paper down position. Pans were removed from the cabinet for weighing and were therefore subjected for short periods to room conditions other than those maintained in the cabinet.

The Series *A* tests were carried out on papers S16 and K31 only. All three desiccants were used, 30 gm. in each pan, or 1 gm. per sq. cm. of test area. Six specimens were taken from each paper. The 12 pans were filled with different desiccants in pairs for each kind of paper, and put into the cabinet for test simultaneously. After enough readings were taken, the desiccant was replaced by another kind, and another test made. For example, six specimens taken from paper K31 were designated as A_1, A_2, A_3, A_4, A_5, and A_6. On the first test run, A_1 and A_2 were filled with magnesium perchlorate, A_3 and A_4 were filled with silica gel, and A_5 and A_6 were filled with calcium chloride. On the second test run, A_1 and A_2 were filled with silica gel, A_3 and A_4 with calcium chloride, and A_5 and A_6 were filled with magnesium perchlorate, and so on to the third run. Each pair of samples was therefore tested with each of the three desiccants in turn, but in different order. It was found possible to analyze the results so as to separate the effect of change of permeance of the papers. Aging effect was taken as the ratio of D_2 to D_1 where D_1 and D_2 are the respective permeances for a particular sample at the beginning of each of two consecutive runs. The aging effect was found to vary from 1.000 to 1.006 and was subsequently ignored in reducing the results since its effect on the calculated value of R_2 amounted at most to no more than 0.6 percentage points.

The general procedure was to establish the value of R_2 for the first acceptable increments of weight gain for each run, based on the averages of the two identical samples in each case, and using magnesium perchlorate as the reference, or standard, desiccant. The variations in R_2 throughout each run were then obtained for successive increments of weight gain established by successive weighings, by comparison with the initial weight gain. The results were then plotted and curves drawn, showing the changes in the apparent relative humidity with gain in weight of the desiccant.

The Series *B* tests were run on all three desiccants and on two papers, F4.9 and K31. After the experience with Series *A* tests, it was decided to run all samples first with magnesium perchlorate as the desiccant, in the paper down position, to establish the "standard" permeance. The desiccants were then replaced and the tests re-run under the desired variations in test conditions. Seventy grams, or 1.2 gm. per sq. cm. of test area of calcium chloride or silica gel, or 60 gm. of magnesium perchlorate were used in each pan. In general this provided a desiccant bed 0.7 in. thick in a pan 1 in. deep.

The 36 pans carrying samples of paper K31 after testing to establish the permeances of the samples were refilled with fresh desiccant. Twelve were filled with calcium chloride, 12 with silica gel and 12 with magnesium perchlorate. Four pans containing each kind of desiccant were then tested in the paper down position, four in the paper up position and four pans of each desiccant were rotated slowly throughout the test.

Only 12 samples of paper F4.9 were tested. This provided only single samples of each desiccant in each of the three pan positions, except in the case of calcium chloride with which duplicate samples were run.

PRESENTATION AND DISCUSSION OF RESULTS

The results of the Series *A* tests with paper K31 are shown in Fig. 4. Owing to the relatively high permeance, there was a weight gain of nearly 1% in the initial period before suitable conditions were established. It was not possible therefore to obtain results at smaller moisture gains.

The results of Series *B* tests with three desiccants, and pans in three different positions, all with paper K31 are shown in Fig. 5. Curves, 8, 11, and 14 may

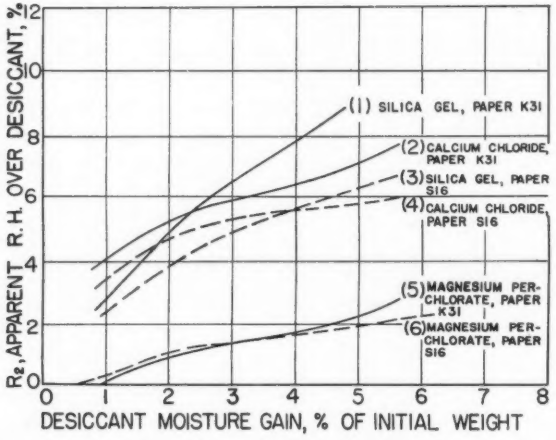
R₂, APPARENT R.H. OVER DESICCANT, %
DESICCANT MOISTURE GAIN, % OF INITIAL WEIGHT
(1) SILICA GEL, PAPER K31
(2) CALCIUM CHLORIDE, PAPER K31
(3) SILICA GEL, PAPER S16
(4) CALCIUM CHLORIDE, PAPER S16
(5) MAGNESIUM PERCHLORATE, PAPER K31
(6) MAGNESIUM PERCHLORATE, PAPER S16

FIG. 4. Apparent relative humidities over three different desiccants, at various moisture gains, for membranes of two different permeances. Series *A* tests.

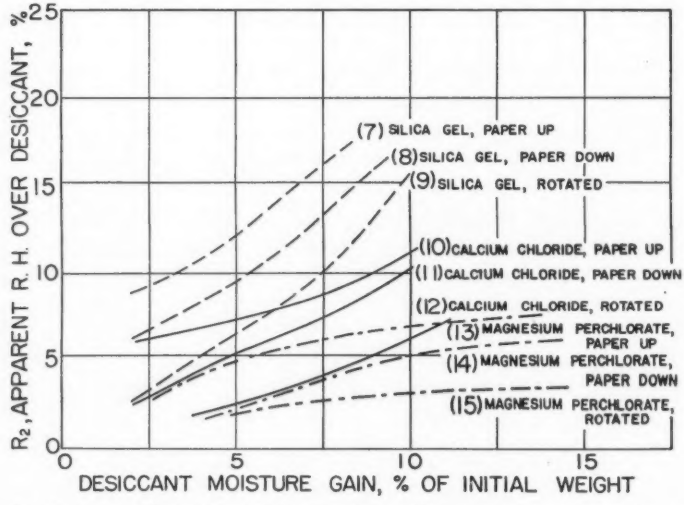
R₂, APPARENT R.H. OVER DESICCANT, %
DESICCANT MOISTURE GAIN, % OF INITIAL WEIGHT
(7) SILICA GEL, PAPER UP
(8) SILICA GEL, PAPER DOWN
(9) SILICA GEL, ROTATED
(10) CALCIUM CHLORIDE, PAPER UP
(11) CALCIUM CHLORIDE, PAPER DOWN
(12) CALCIUM CHLORIDE, ROTATED
(13) MAGNESIUM PERCHLORATE, PAPER UP
(14) MAGNESIUM PERCHLORATE, PAPER DOWN
(15) MAGNESIUM PERCHLORATE, ROTATED

FIG. 5. Apparent relative humidities over three different desiccants, at various moisture gains, for three pan positions and a 31 perm membrane. Series *B* tests.

be compared directly with Curves 1, 2, and 3 of Fig. 4. Curves 1 and 8 for silica gel and Curves 3 and 14 for magnesium perchlorate check very well. The results for calcium chloride in the Series *B* tests are similar to those for the Series A tests, but are only about 75% as great at the same moisture gains. A variation of about 2% in initial moisture content could have accounted for this, but it seems possible that the unavoidable disturbance of the desiccant in handling and weighing in Series *B* tests also had an effect. The actual plotted points to which the curves were drawn by observation are shown only in Fig. 2 for Curves 7, 8, and 9 for silica gel. The scatter of points shown in Fig. 2 may be regarded as typical, and in most cases there was little difficulty in establishing the curve to within 1% apparent relative humidity. This must be regarded as a satisfactory condition, in view of the fact that individual points were calculated from small differences in consecutive weighings.

In every case, the effect of rotating the pans is shown to decrease the apparent relative humidity, R_2, while testing in the paper up position yields a higher result than does the paper down position. Similar results are shown in Fig. 6

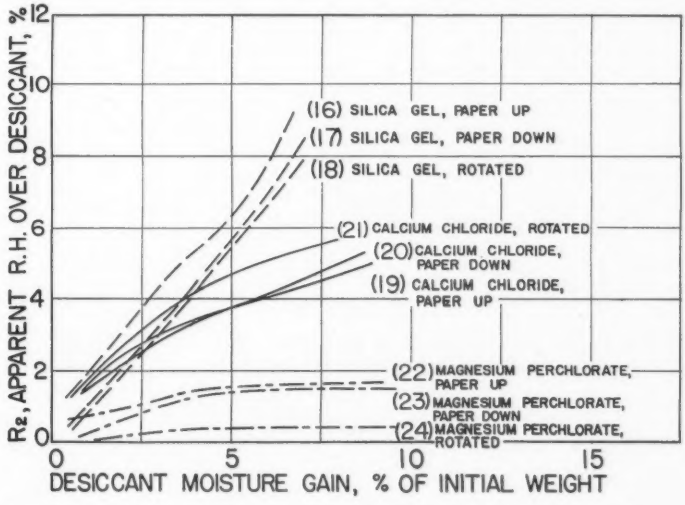

FIG. 6. Apparent relative humidities over three different desiccants, at various moisture gains, for three pan positions and a 4.9 perm membrane. Series *B* tests.

for paper F4.9 except in the case of calcium chloride in which the rotated tests showed the highest values. This is thought to be due to the accumulation of a fairly dense layer of desiccant dust which was formed on the back of the rough felt as a result of the tumbling during rotation. This did not occur with the other desiccants, and did not occur with calcium chloride in the case of the smoother papers.

The differences in apparent relative humidity as between paper up and paper down tests may be attributed mainly to the extra resistance presented by

the air layer to diffusion of vapor in the paper up tests. The curves for the two cases are shown to be roughly parallel and to differ by 2 to 3% for the high rate provided by paper K31 and by less than 1% for the lower rate of paper F4.9.

A theoretical equation for the pressure gradient to maintain diffusion of one gas through a second, stagnant gas is given by Sherwood (10) as

$$\Delta P/\Delta X = N_A RT P_{BM}/DP$$

where $\Delta P/\Delta X$ = gradient of diffusing gas pressure in atmospheres per cm.

N_A = Gram molecules of gas diffused through unit area of 1 sq. cm. in 1 sec.

R = Gas constant, cubic meters per deg. K.

T = Temperature, deg. K.

P_{BM} = Logarithmic mean value of the stagnant gas pressure, atm.

P = total pressure, atm.

D = diffusion constant, cm.^{2} per sec.^{2}

When this equation is applied to the conditions of the tests of Fig. 4, the following values may be used:

Average gain of 0.045 gm. per hour through 57.5 sq. cm.,

$N_A = 1.21 \times 158$ gm.-mol. per cm.^{2} sec. Average thickness of air layer 0.75 cm.

D = 0.219 cm.^{2} per sec.^{2} for water vapor in air (see Jost (5)).

R = 82.07.

The vapor pressure drop ΔP, through the air layer is found to be 0.00995 atm., or 0.0298 in. Hg, corresponding to 3.6% relative humidity. The equation is linear with respect to N_A, the rate of flow, and therefore would predict a pressure drop of 0.6% relative humidity across the air layer in the case of paper F4.9 for which the flow rate is about one-sixth of that for paper K31. The agreement of these values with the test data is reasonably good.

The curves for each desiccant have been redrawn in Fig. 7 to show the effect of the flow rates obtained for the three different papers. The equilibrium condition curves indicated by the data of Table I have also been drawn in. As might be expected, the higher rates of flow are shown to produce higher apparent relative humidities on the desiccant side, and all of these are above the equilibrium data. The data for calcium chloride appear to provide an exception but only if Series *A* and Series *B* data are compared. As previously noted, all the Series *A* tests with calcium chloride gave higher values than Series *B* and subsequent tests.

The range of membranes to be tested may vary from less than 0.1 perms to as much as 100 perms. The majority of membranes to be used to restrict vapor flow will fall below 2 perms. A permeance of 1 perm at cabinet conditions of 73.5°F. and 50% relative humidity, with 1 gm. of desiccant provided per sq. cm. of membrane area leads to an increase in desiccant moisture during test of 0.07% per day. The duration of a test is usually determined by the time required for adjustment of the membrane to test conditions plus from

5 to 10 equal time intervals each of sufficient duration to ensure weight increases large enough to be determined accurately in weighing. The total gain during tests of membranes having permeances less than 1 perm will seldom exceed 1%. However, if the permeance is 30, and daily weighing is used, the weight gain per day will be about 2%, and after a minimum of five daily weighing periods the total gain will be 10%. No tests were carried out on

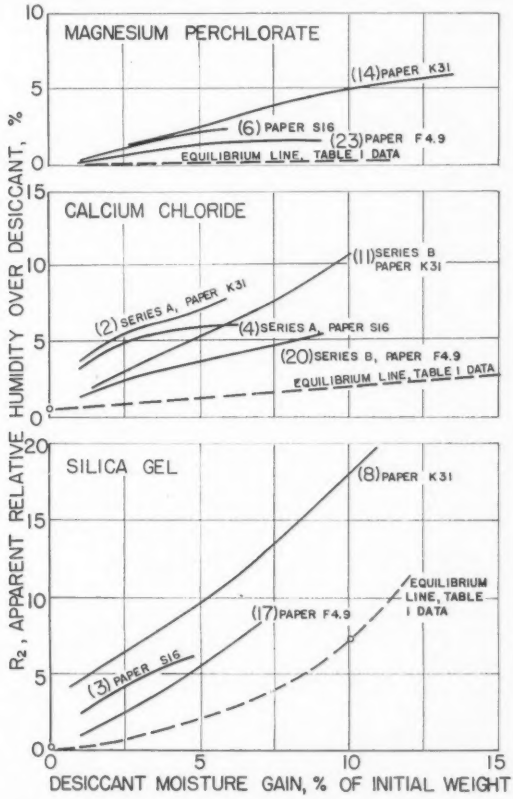

FIG. 7. Apparent relative humidities at various moisture gains, for each of three desiccants, with membranes of different permeances and pans in the paper-down position.

low-permeance membranes because of the long test periods required to obtain satisfactory increases in desiccant moisture, and the results shown apply in practice mainly to the testing of membranes of moderate and high permeance. For these cases, the calcium chloride and silica gel used are shown to provide apparent relative humidities up to 4% above magnesium perchlorate even at moisture gains as low as 1 and 2%. The silica gel, however, showed a loss in weight on heating at 200°C. of 1½% and the calcium chloride lost about 8½%. If these be taken as the true initial moisture contents then 2% moisture

gain corresponded to an average moisture content, dry basis, of 3½% for the silica gel and 10½% for the calcium chloride.

The silica gel tested is shown to provide little margin of safety in dry pan testing even if it is to be dried initially and if a 5% limit of relative humidity is to be tolerated. Silica gel, unlike the other two, is an adsorbent and depends on sorption by a large surface area. The effective surface area for sorption undoubtedly varies with the source of the material. It is not known whether the material tested was a representative product. However the relative effectiveness of various samples of silica gel could be readily assessed for practical purposes by a test procedure similar to that used here.

Both the calcium chloride and magnesium perchlorate are classed as absorbents, and take up water mainly as water of hydration. Their performance as desiccants might therefore be expected to be somewhat more reliable in view of the definite amounts of water involved in adding successive molecules of water to each molecule of substance. For the materials as tested, the magnesium perchlorate was shown to be superior to the calcium chloride, taking on about 10% of water at the 31 perm rate, in the paper down position of test, before a 5% level of apparent relative humidity was exceeded, as compared to from 2 to 5% for the calcium chloride. However, if it be assumed that the magnesium perchlorate was anhydrous as stated, and that the calcium chloride already had 8½% moisture at the start of the test, the performance of the calcium chloride is shown to be relatively good. This was considered to be of some importance, not only in view of the lower cost of calcium chloride and greater availability in most laboratories, but also because it appeared from the drying tests carried out that calcium chloride could be readily and successfully dried before use to a known initial moisture condition. Further tests with calcium chloride were therefore carried out to compare the performance with and without initial drying.

A supply of calcium chloride was divided, and half of it dried as before at 200°C. for 24 hr. The loss in weight was 9%, dried basis. Tests were then carried out, as in the Series *B* tests, using only paper K31, but using both dried and undried calcium chloride, with pans arranged for paper down and rotated conditions, with a third set tested in the paper down position, but shaken each day. Four pans were tested for each set of conditions. The results obtained are shown in Fig. 8. Curve 27 for the undried but rotated material is almost identical to Curve 26 for the dried material, but shifted to the left by 9%, the moisture removed in drying. The changes in slope of both curves at the points corresponding to one water molecule added throughout (17% moisture content) and two water molecules added (33% moisture content) are very marked. (Powers (9) shows a number of similar curves for chemical compounds in Portland cement pastes.) The 5% level of relative humidity is not reached until the moisture content exceeds 18%. Curve 25 for the samples shaken each day shows apparent relative humidities which do not exceed those for the rotated and dried condition by more than 1% until a moisture content of 25% is reached, and also shows the changes in slope at 17% and 33%

moisture gain. Curve 28 for the paper down, dried tests does not show the slope changes and is everywhere much above the other curves for the dried material. The 5% level of relative humidity is reached at about 8% moisture content, while for the undried material tested under the same conditions the 5% level of relative humidity is reached at slightly over 5% moisture gain. The apparent increase in moisture capacity at the 5% level of humidity,

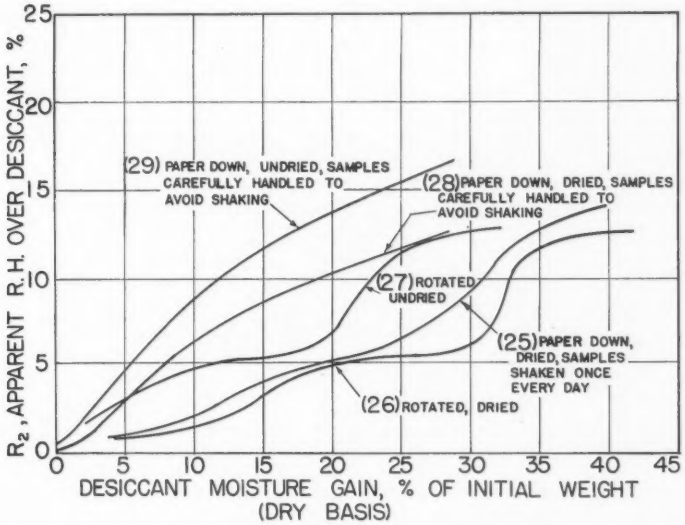
R_2, APPARENT R.H. OVER DESICCANT, %
25
20
15
10
5
0
0 5 10 15 20 25 30 35 40 45
DESICCANT MOISTURE GAIN, % OF INITIAL WEIGHT
(DRY BASIS)
(29) PAPER DOWN, UNDRIED, SAMPLES CAREFULLY HANDLED TO AVOID SHAKING
(28) PAPER DOWN, DRIED, SAMPLES CAREFULLY HANDLED TO AVOID SHAKING
(27) ROTATED UNDRIED
(25) PAPER DOWN, DRIED, SAMPLES SHAKEN ONCE EVERY DAY
(26) ROTATED, DRIED

FIG. 8. Apparent relative humidities at various moisture gains for calcium chloride as received and after drying, with a 31 perm membrane.

due to drying, is about 2½%, increasing at the 12% level of humidity to about 10%, whereas in the rotated tests, the increase was about equal throughout to the moisture removed in drying. This difference, as well as the absence of slope changes at 17% and 33% moisture contents may be attributed to the gradient conditions of moisture content built up in the desiccant bed when the pans are undisturbed.

Drying the calcium chloride brings its performance well within 1% in humidity of the condition maintained by the magnesium perchlorate at low moisture gains, and increases its moisture holding capacity in the paper down position with paper K31 to nearly 8% at the 5% level of humidity as compared to 10% for the magnesium perchlorate. When shaken, the corresponding moisture capacity for calcium chloride is 19% and when rotated is 23%. The corresponding data for magnesium perchlorate were not obtained, since the moisture gains were not carried far enough, and no shaking was attempted, but similar increases might be expected.

Calcium chloride, when dried, is shown to be nearly as good for dry pan test purposes, as magnesium perchlorate. In addition, it has the advantage

that drying can readily and safely be carried out, so that the initial moisture content can be predetermined at the start of a test. When the moisture content of calcium chloride reaches 98%, for six added molecules of water, it becomes liquid. This characteristic may lead to impregnation of a sample by liquid desiccant at high moisture contents. Some care must therefore be exercised in using calcium chloride especially when, in special investigations, the same membrane is re-used, with fresh desiccant. Desiccant dust adhering to the membrane must not be exposed for any appreciable time to moist air conditions.

The calcium chloride desiccant used was appreciably affected in its physical appearance, by the tumbling resulting from rotation. Fig. 9 shows the appearance of fresh desiccant, of desiccant shaken each day, and of desiccant after rotation. In the two latter cases the desiccant had taken on a moisture content of about 40%, corresponding to about 20 days of test. With rotation, the desiccant dust has a marked tendency, as may be noted, to adhere and form a layer on the edges of the test dish. When the paper is rough, a coating will also form on it, leading to some modification of the over-all performance. The larger particles of desiccant, meanwhile, tend to become rounded, as may be seen, and no doubt also are partly modified in shape by fines adhering to them. This effect was not particularly noticeable in the case of the other two desiccants. No increase in permeance attributable to the scouring action of the tumbling desiccant was found for the three papers tested although a fourth paper with surface coating which was largely responsible for its resistance to vapor flow was substantially increased in permeance.

Shaking is shown by the tests on calcium chloride to be an acceptable substitute for continuous rotation. This was carried out once each day when, with paper K31, the moisture gain was about 2% per day.

The results obtained with calcium chloride, and especially the ability shown to detect the 17% and 33% moisture levels would again indicate the possibility of employing procedures similar to those followed here for the practical assessment of desiccants for certain purposes.

CONCLUSIONS

1. All three desiccants tested provided much higher apparent relative humidities behind the test membrane in the dry pan test than the equilibrium values commonly quoted for them.

2. The apparent relative humidity maintained increases with the rate of flow, corresponding to increased membrane permeance, and with increased moisture content of the desiccant.

3. An air film of appreciable thickness maintained between the desiccant and the test membrane as in the paper up pan position will lead to increased relative humidities behind the test membrane corresponding in magnitude to the vapor pressure differences required to maintain diffusion through the air film. These differences increase with increasing film thickness and rate of vapor flow.

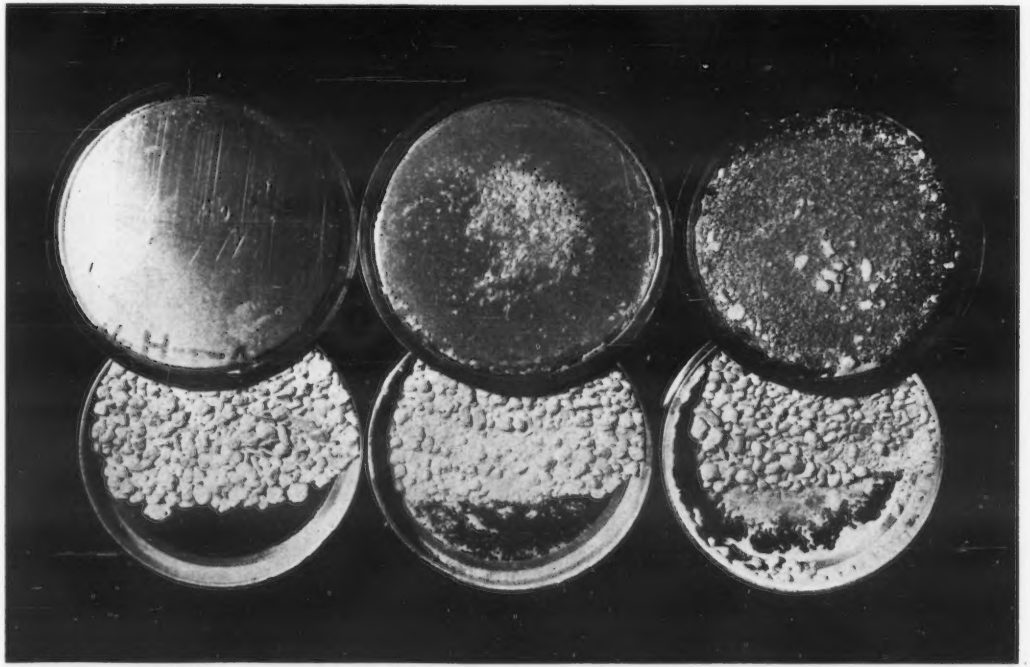

FIG. 9. Pans with bottoms removed, showing, left to right, calcium chloride as received, and as it appeared at 40% moisture content after daily shaking and after rotation.

4. Gradient conditions in the desiccant bed lead to increased relative humidities behind the membrane. The effect of these can be greatly reduced, if not eliminated, by rotating the pan during test, so as to provide continuous agitation of the desiccant. Results almost as satisfactory, with less risk of changing the physical structure of the desiccant, or of damage to the membrane, can be achieved by periodic shaking of the test pans.

5. The only adsorbent tested, silica gel, did not perform as well as the absorbents, calcium chloride and magnesium perchlorate. A 5% limit on inside humidity might frequently be exceeded under conditions encountered in dry pan testing, with the silica gel material tested.

6. The calcium chloride used was shown to be almost as effective as anhydrous magnesium perchlorate provided that it was dried before use.

7. The use of a desiccant which can be dried to a known moisture condition before use is to be recommended.

8. The procedure followed here, using essentially the dry pan method of test, with a standard membrane, would appear to have value in the assessment of solid sorbents for use in certain practical drying applications.

ACKNOWLEDGMENT

This investigation was carried out as a research project within the Department of Mechanical Engineering, University of Saskatchewan. It represents a contribution to a program of cold-weather wall research being carried out cooperatively by the University of Saskatchewan and the Division of Building Research, National Research Council.

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A NOTE ON THE STABILITY OF VITAMIN A IN CANADIAN MARGARINE[1]

By T. K. Murray and J. A. Campbell

ABSTRACT

Samples of margarine from the current production of 13 manufacturers have been stored for 12 months at room temperature and at 5°C., and their vitamin A content determined at intervals. The results indicate that after 12 months' storage at room temperature, 10 of the 13 products still met or surpassed label claim for vitamin A. These samples lost an average of 10% of their vitamin A content during storage. After 12 months' storage at 5°C. the same 10 samples had lost only 1.7% of their vitamin A. Peroxide numbers of stored samples indicated that there was significant correlation between loss of vitamin A and oxidative changes in the margarine.

In 1951 this laboratory published the results of a study (2) on the composition of Canadian margarine, including the vitamin A content. It was concluded at that time that only a very small percentage of the Canadian production failed to meet the label claim for vitamin A. Since that time the question of stability of the vitamin A in Canadian margarine has arisen and it was decided to study this problem at both room temperature and under refrigeration. This paper presents the results of this study.

EXPERIMENTAL

Ten 1 lb. samples of the current production of 13 margarine manufacturers were purchased by inspectors of the Food and Drug Divisions during October 1951. Vitamin A determinations, using the antimony trichloride method of Rice, Primm, and Coombes (3), were carried out on duplicate 1 lb. samples of the fresh margarine. Six 1 lb. samples of each brand were then stored at room temperature (23°–28°C.) and two 1 lb. samples of each were stored at 5°C. Vitamin A determinations were carried out on duplicate 1 lb. samples of the room temperature series at intervals of three months, for one year. For the vitamin A determination, samples of 10 gm. were obtained from within individual pound packages by boring through one-half the length of the block. At the end of 12 months the refrigerated samples were also assayed. Peroxide numbers were determined by the method of Lea (1) on the fresh samples and on other samples after 12 months' storage at both room temperature and 5°C. For this determination, samples of 1 gm. were obtained from the inner portions of individual pound packages. Moisture losses were of the order of 3 to 5% and were not considered of sufficient magnitude to require the adjustment of vitamin A content or peroxide numbers.

RESULTS AND DISCUSSION

The detailed results of this study are shown in Table I. Analysis of the fresh samples showed that only one manufacturer, of the 13 included in this study,

[1] *Manuscript received May 4, 1953.*
Contribution from the Food and Drug Laboratories, Department of National Health and Welfare, Ottawa, Canada.

TABLE I

VITAMIN A CONTENT OF MARGARINE IN I.U./100 GM.*

Mfr.	Months at room temperature					Months at 5°C.
	0	3	6	9	12	12
A	4510	4190	3930	3950	3920	4190
B	4410	4280	4050	4010	3830	4150
C	4360	3890	4150	4050	3450	4200
D	4200	4240	4130	3850	3800	4040
E	4120	3990	3960	3490	3550	4030
F	4020	4080	3860	3820	3790	4140
G	3960	3930	3910	3630	3560	3860
H	3950	4160	4040	4290	3960	4300
I	3920	4160	3730	3780	3630	4080
J	3860	3670	3740	3670	3660	3630
K	3390	2760	—	1580	1390	2790
L	3330	2010	700	620	300	1330
M	3020	2800	2530	2250	1710	2760

**Labelled potency is 3525 I.U./gm. or 16,000 I.U./lb. with the exception of Samples A and H which are labelled at 4000 I.U./gm.*

produced margarine which was significantly below label claim. This is an improvement over the previous year when five brands of 15 examined did not meet label claim. No one brand was deficient in vitamin A content for both years. The average vitamin A content of the 12 products which met label claim was 4000 I.U./100 gm. which agreed well with the 4060 I.U./100 gm. reported in the previous study.

After one year's storage at room temperature 10 products still met or surpassed label claim. The three samples which showed marked decreases in vitamin A content were considerably below the average vitamin A content at the beginning of the test. They represented only a very small proportion of the total production. The average vitamin A content of those samples which still met label claim after one year's storage at room temperature was 3720 I.U./100 gm. which is a decrease, for those samples only, of 10%. Sample H and possibly sample C appeared somewhat less uniform in composition than the other samples. In the refrigerated series the same 10 samples met or surpassed label claim after one year. The average vitamin A content of these samples after one year of refrigerated storage was 4060 I.U./100 gm. or a decrease in potency of 1.7%.

The results of the peroxide determinations with the corresponding loss of vitamin A are shown in Table II. A statistical analysis of these data indicated that there was a correlation between the peroxide number and vitamin A destruction. Values of r were 0.62 for the room temperature series and 0.91 for the refrigerated group.

It can be concluded from this study that the vitamin content of Canadian margarine is relatively stable over at least one year, even when stored at room temperature. The decrease in vitamin A content is correlated with the increase in peroxide number.

TABLE II

LOSS OF VITAMIN A AND THE PEROXIDE NUMBERS OF SAMPLES OF MARGARINE STORED FOR 12 MONTHS AT ROOM TEMPERATURE AND AT 5°C.

Stored at room temperature		Stored at 5°C.	
Vitamin loss I.U./100 gm.	Peroxide number	Vitamin loss I.U./100 gm.	Peroxide number
0	7.5	0	3.6
200	11.3	0	4.7
230	6.3	0	4.1
260	27.5	90	6.4
290	6.5	100	5.1
400	14.0	160	5.1
400	7.7	160	6.5
570	22.5	180	7.1
580	14.8	260	11.7
590	36.3	260	8.2
910	9.1	320	22.9
2000	11.8	600	14.3
3000	52.8	2000	36.7

ACKNOWLEDGMENT

The authors are indebted to Mr. P. Lichon for much of the vitamin A analysis reported here.

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THE FATTY ACID COMPOSITION OF CARAGANA SEED OIL[1,2]

By L. N. Cole[3] and B. M. Craig[4]

ABSTRACT

The seed of the shrub *Caragana arborescens* contained 11.8% of a reddish colored oil with the following characteristics, iodine value 141.7, saponification value 185.9, n_D^{25} 1.4744, and unsaponifiable matter 2.9%. The oil had the following fatty acid composition: palmitic 3.1, stearic 6.2, arachidic 1.0, behenic 2.9, hexadecenoic 0.2, oleic 6.2, eicosenic 0.2, linoleic 67.1, and linolenic 2.3%. The saturated acids were identified by isolation of the methyl esters whereas oleic and linoleic acids were identified by conversion to dihydroxy and tetrabromo compounds respectively.

The component acids of some 500 seed fats have been investigated and elucidated by a number of different workers. However, the oil from the caragana shrub has hitherto remained unnoticed.

The caragana shrub is a member of the Leguminosae and is indigenous to Siberia and China. Two main species are known, *Caragana chamluga* and *Caragana arborescens*, the former being native to China and the latter to Siberia.

The shrub is used in Canada as a hedge or border plant and has not found any other commercial importance.

MATERIALS AND METHODS

The seed used in the present investigation was a composited sample of varieties of *Caragana arborescens* obtained from the Dominion Forestry Farm, Sutherland, Sask. The seed was finely ground and extracted for 40 hr. in an enlarged Soxhlet apparatus using Skellysolve "F" (b.p. 30–50° C.) as a solvent. The solvent was removed by distillation *in vacuo*.

The oil was divided into three portions which were treated as follows:

(*a*) Converted to methyl esters and completely hydrogenated using Raney nickel as a catalyst.

(*b*) Unsaponifiable matter removed by saponifying the glycerides, extracting the unsaponifiable matter from the ethanol–water mixture with ethyl ether, and conversion of the soaps to methyl esters by the dimethyl sulphate procedure.

(*c*) Converted to methyl esters without prior removal of unsaponifiable matter.

The methyl esters were prepared according to the dimethyl sulphate procedure outlined by Youngs and Craig (10) with the following modification.

[1] *Manuscript received June 3, 1953.*

Contribution from the National Research Council of Canada, Prairie Regional Laboratory, Saskatoon, Sask. Issued as Paper No. 158 on the Uses of Plant Products and as N.R.C. No. 3047.

[2] *Presented to Graduate School, University of Saskatchewan, in partial fulfillment for Master of Science degree.*

[3] *Graduate student, University of Saskatchewan. Present address: Medical College, Ohio State University, Columbus 10, Ohio.*

[4] *Assistant Research Officer.*

The excess potassium hydroxide in the saponification mixture was neutralized by bubbling carbon dioxide into the reaction flask. This procedure eliminated the use of methanolic hydrogen chloride and filtration of the potassium chloride.

The methyl esters were distilled in a 25 mm. × 36 in. Heli-grid Podbelniak column at a head pressure of 10 mm. and a pressure drop across the column of 15 mm. of mercury. Spectrophotometric analyses were made according to the modified Swain and Brice (9) procedure using a Beckmann DU spectrophotometer. Iodine values were measured by the Wijs method using one hour reaction time and a 0.1 *N* solution of sodium thiosulphate. Saponification values were measured by the official method (1) where the samples were sufficiently large and by the method proposed by Marcali and Rieman (6) for smaller samples. The latter method was checked on large samples against the official method and was found to give reliable results. A Bausch and Lomb refractometer equipped with a controlled temperature bath was used to measure refractive indices.

RESULTS

Fatty Acid Composition

The caragana seed contained 11.8% of a reddish colored oil with the following characteristics, iodine value 141.7, saponification value 185.9, n_D^{25} 1.4744, n_D^{55} 1.4646, and unsaponifiable matter 2.9%.

The hydrogenated methyl esters were distilled first using an added known quantity of purified methyl behenate as a "chaser". The distillation curve is shown in Fig. 1. Four fractions are evident from this curve and the boiling

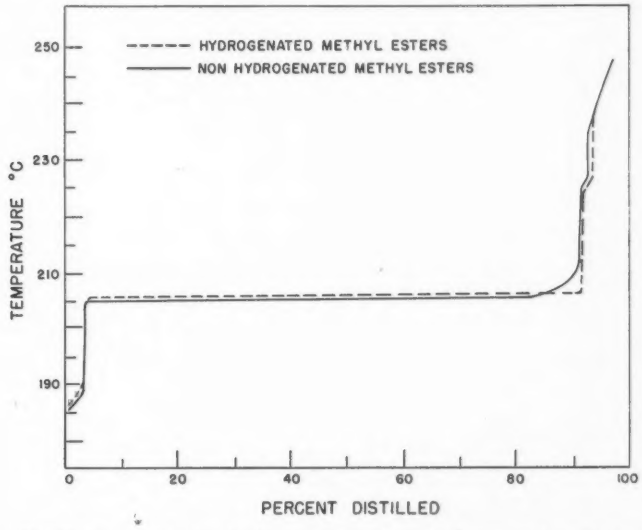

FIG. 1. Distillation curves for hydrogenated and nonhydrogenated methyl esters from caragana seed oil.

points correspond to those found for C_{16}, C_{18}, C_{20}, and C_{22} methyl esters. The separation into fractions is clearly defined and the data from this distillation were used to estimate "carry over" in the distillation of the unsaturated esters.

The methyl esters from which the unsaponifiable matter was removed were distilled using methyl behenate as a "chaser". A weighted total on iodine value and refractive index showed a loss of 8.4 and 0.0013 units respectively. This extensive loss of unsaturation made an accurate computation of the fatty acids impossible.

The methyl esters containing unsaponifiable matter were distilled using methyl behenate as a "chaser", and the distillation curve is shown in Fig. 1. The methyl behenate was added after 82% of the esters were distilled. An aliquot was removed from the still pot prior to addition of the chaser and a weighted total on iodine values and refractive indices of the fractions at this point showed no loss in unsaturation. The fractionation was continued until the boiling point and per cent distilled indicated that a portion of the added methyl behenate had been collected.

There is good agreement with the distillation curve for the hydrogenated esters which indicate very little carry-over of the unsaturated esters between fractions of different chain lengths. A second weighted total on iodine value and refractive index at the end of the distillation showed no loss of unsaturation. These data are presented in Table I and saponification values and naturally conjugated diene and triene contents are included.

TABLE I

MATERIAL BALANCE ON DISTILLATION OF METHYL ESTERS

Characteristic	Original oil	Methyl esters	Methyl* esters	Weighted total from distilled fractions
Weight		306.6 gm.		304.8 gm.
Iodine value	141.7	140.8	140.7	140.6
n_D^{55}	1.4646	1.4667	1.4460	1.4460
Saponification value	185.9	185.8	185.5	185.1
Unsaponifiable	2.89	2.90	0	2.92
Monoene acids	15.27	14.15	17.35	17.40
Diene acids	71.18	71.26	68.64	67.12
Triene acids	1.96	1.97	2.37	2.25
Saturated acids	11.59	12.62	11.64	13.23

* *Methyl esters with unsaponifiable matter removed.*

The analyses of the distilled fractions are given in Table II. Fraction 5 is made up of three distilled fractions which were identical in refractive index and were mixed together. The amounts of di- and triethenoid fatty acids were determined by spectral analyses. The monoethenoid acids were calculated by difference from the iodine value of the sample and the calculated iodine value of the di- and triethenoid acids. The saturated acids were then determined by the difference between the total fatty acids and the unsaturated fatty acids.

The C_{18} acids which occur in Fractions 3, 4, 5, and 6 show a concentration of linoleic acid in the first fractions and a concentration of stearic acid in the last fractions. The triene acid content shows a marked increase in Fraction 6 but this was measured mainly as naturally conjugated triene. The naturally conjugated triene in Fraction 7 was also relatively large. Fraction 9 showed a boiling point, refractive index, and saponification value which were almost identical to the values for methyl behenate.

The fatty acid distribution in the fractions and the total composition for the oil are given in Table III. These data were calculated from Table II. Fractions 1 and 2 were considered from the boiling point, refractive index, and saponification value to be mainly C_{16} acids. The diethenoid and triethenoid acids were considered to be linoleic and linolenic rather than the corresponding hexa-

TABLE II

ANALYSES OF DISTILLED FRACTIONS

Fraction	B.p., ° C. at 10 mm.	Weight, %	Iodine value	Saponification value	n_D^{55}	Monoene, %	Diene, %	Triene, %	Sat'd, %
1	176–186	0.9	14.3	208.2	1.4319	7.2	3.3	0.6	84.2
2	186–190	2.5	13.3	203.5	1.4295	4.7	3.5	0.8	86.3
3	190–205	13.6	150.0	192.1	1.4460	15.3	74.2	0.4	5.4
4	205	15.9	155.5	190.4	1.4464	17.3	75.6	0.4	2.0
5	205	49.0	151.2	190.0	1.4460	16.8	69.9	2.2	6.4
6*	205–210	8.6	126.5	188.6	1.4442	28.8	50.4	3.3	12.8
7*	210–235	2.9	105.8	182.0	1.4470	16.2	37.6	8.4	33.1
8*	235–248	2.3	3.2	162.2	1.4415	0	7.8	1.8	85.7
9*	248**	1.4	0.9	158.3**	1.4361**	0	0.7	0.1	94.5
Unsaponifiable		2.9							

* *Percentage corrected for aliquot removed during distillation.*

** *Methyl behenate, b.p. 248° at 10 mm., saponification value 158.25, n_D^{55} 1.4359.*

TABLE III

DISTRIBUTION OF FATTY ACIDS IN DISTILLED FRACTIONS

Fatty acid	Fraction						Total
	1	2	3, 4, 5	6	7	8, 9	
Palmitic	0.79	2.33					3.12
Hexadecenoic	0.06	0.13					0.19
Stearic			5.58	0.58			6.16
Oleic			16.72	0.28			17.00
Linoleic	0.03	0.10	65.59	1.17	0.13	0.10	67.12
Linolenic	0.02	0.01	1.63	0.26	0.33		2.25
Arachidic				0.42	0.58		1.00
Eicosenoic				0.21			0.21
Behenic					1.49	1.46	2.95
							100.00

decanoic acids. The samples were too small to permit identification of these unsaturated acids.

Fraction 7 was calculated as a mixture of C_{18} and C_{20} acids from the saponification value. The diethenoid acid was identified as linoleic by conversion to the tetrabromide. The diethenoic and triethenoic acids in Fractions 8 and 9 were likewise considered to belong to the octadecanoic series as the samples were too small to permit an identification of these unsaturated acids.

Identification of Fatty Acids

The major component acids of the Fractions in Table II were further identified in the following manner:

Palmitic acid—isolated from Fractions 1 and 2 by fractional crystallization of the methyl esters from acetone at −12° C. The white precipitate was recrystallized from acetone and had a melting point 30.0–30.4° C. (m.p. methyl palmitate 30.1° C. (4)).

Stearic acid—isolated by fractional crystallization of the fatty acids formed on hydrolysis of Fraction 5 from acetone at −12° C. The precipitate was recrystallized and had a melting point of 69.6° C. (m.p. stearic acid 69.6° C. (4)).

Arachidic acid—the methyl esters of Fraction 7 were crystallized from acetone at −12° C. The precipitate had a melting point of 43° C. (m.p. methyl stearate 39.1° C., methyl arachidate 46.6° C. (4)). The precipitate was considered to be a mixture but the sample was too small to obtain a separation of the two esters.

Behenic acid—isolated from the methyl esters of Fraction 9 by fractional crystallization. The compound was recrystallized and had a melting point of 53.2° C. (m.p. methyl behenate 53.3° C. (4)).

Oleic acid—isolated as dihydroxystearic acid from Fraction 5. A portion of this fraction was converted to the free fatty acids from which the stearic acid was crystallized. The liquid portion was then brominated in petroleum ether (Skellysolve F). After removal of the tetrabromides the filtrate was debrominated and oxidized with performic acid by a combination of the methods of Swern *et al.* (8) and Fitelson (3). The acid produced by this oxidation had a melting point of 94–95.2° C. (m.p. dihydroxystearic acid 95° C. (3, 5)).

Linoleic acid—isolated as the tetrabromide from Fraction 5 as given above. The tetrabromo derivative had a melting point of 114.7–115.5° C. after recrystallization (m.p. tetrabromostearic 114.5–115.2° C. (2)). The same bromo adduct was isolated from Fraction 7.

Linolenic acid—could not be isolated as the pure hexabromide. It was believed that the presence of the relatively large quantity of tetrabromide made the fractional crystallization of this hexabromide very difficult.

DISCUSSION

The use of methyl behenate as a "chaser" facilitated the complete distillation of C_{16}, C_{18}, and C_{20} fractions of the esters. This technique however does not reveal higher homologues, but the weighted totals of iodine values, saponifi-

cation values, and refractive indices indicate that such members, if present, existed in only trace amounts. The technique does not complicate the calculation of fatty acid composition as the amount of chaser is accounted for first.

The removal of unsaponifiable matter apparently contributed to thermal destruction of the unsaturated esters, particularly the diethenoid and triethenoid series. In addition it is known that the presence of unsaponifiable matter interferes with spectral analyses in the ultraviolet region (7), and it was believed that a removal of this material prior to distillation would improve the accuracy of the analysis. It is evident from Table I that there is good agreement for the fatty acid analyses between the total from the fractions and the gross analysis of the methyl esters with unsaponifiable matter removed. There is better agreement between the fatty acid analysis for the whole oil and methyl esters containing unsaponifiable matter. However the agreement between material containing unsaponifiable matter and that from which unsaponifiable matter is removed is not good.

The fatty acid composition given in Table III is on the basis of total fatty acids. Caragana seed oil appears to have a fatty acid composition similar to that of other vegetable oils of the semidrying class. An unusual feature of the oil is the relatively high quantity of unsaponifiable matter. This material has not been investigated further.

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THE FATTY ACID COMPOSITION OF SAFFLOWER SEED OIL[1]

By B. M. Craig[2]

ABSTRACT

The fatty acid compositions of safflower seed oil from seed of the Indian variety grown in North Dakota, U.S.A., and at Saskatoon, Sask., were determined. The oil was converted to methyl esters which were fractionated by distillation and the fractions were analyzed for component acids. The results show a higher saturated acid and lower oleic acid content than has been reported previously in the literature. Linolenic acid is present in only very small amounts.

The fatty acid compositions of the oil from safflower seed grown in various countries have been investigated by a number of workers (1, 2, 4, 5, 8, 9). The reported relative amounts of the fatty acids have varied considerably but the content of oleic acid has always been greater than the total amount of saturated acids. Variations from 0 to 3% have been reported for the amount of linolenic acid. In the course of some survey work on safflower seed oils, this laboratory found values for oleic acid which were lower than any reported in the literature. An investigation of the fatty acid composition of safflower seed oil was undertaken to check this observation.

MATERIALS AND METHODS

Two samples of safflower seed of the Indian variety were used in the present investigation. The first sample had been grown in North Dakota, U.S.A., and was obtained from the Co-operative Vegetable Oil Mills Ltd., Saskatoon, Sask. The second sample was obtained one year later from Dr. B. C. Jenkins, University of Saskatchewan. This crop was grown on the University Farm from the seed mentioned above.

The seed was dehulled in an impact huller and the meats were finely ground and extracted with Skellysolve "F" in a Soxhlet type of extractor. The solvent was removed from the oil by distillation *in vacuo*.

The oil was converted to methyl esters in quantitative yield (99.7%) by the dimethyl sulphate procedure (10) with the modification that carbon dioxide gas was used instead of methanolic hydrogen chloride to neutralize the excess potassium hydroxide used in the saponification of the glycerides. The esters were distilled in a Podbelniak Heli-Grid fractional distillation unit at a pressure of 10 mm. of mercury. Purified methyl behenate was used as a "chaser" to facilitate complete distillation of the methyl esters from the safflower seed oil. Previous work (6, 11) has shown that an adequate separation on the basis of chain length is obtained with this unit. A more efficient separation was obtained with the second sample of esters by continuous evacuation of the vacuum jacket on the fractionation column with an oil diffusion pump.

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[2] *Assistant Research Officer.*

The distilled fractions were analyzed for component acids by iodine value, ultraviolet absorption, saponification value, and refractive index in the same manner as described in a previous publication (3).

RESULTS

The unsaponifiable matter was removed from a portion of the first sample of safflower seed oil by converting the glycerides to soaps and extracting the alcoholic solution with ether. The soaps were acidified and converted to methyl esters which were distilled. The weighted totals of iodine values and refractive indices for the fractions showed an extensive loss of unsaturation and indicated that a removal of unsaponifiable matter prior to distillation was undesirable. This observation corroborated similar work on caragana seed oil performed in this laboratory (3).

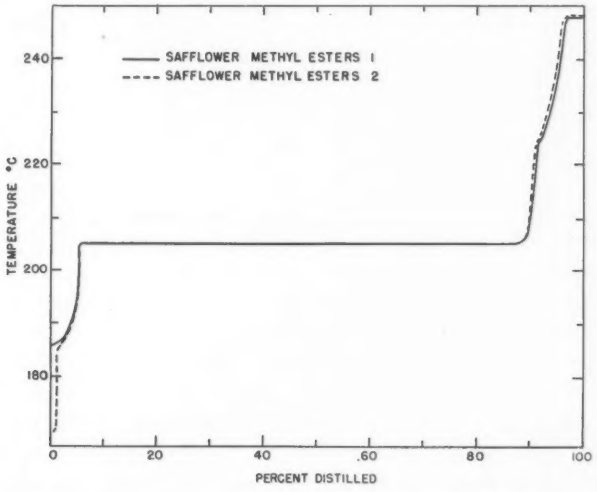

FIG. 1. Distillation curves for methyl esters of safflower seed oil.

The distillation curves for the two samples of esters are shown in Fig. 1. The methyl behenate was added to Sample 1 after the major portion of the C_{18} material was distilled. An aliquot was removed from the still pot and a weighted total of iodine values and refractive indices at this point in the distillation showed no loss of unsaturation. The distillation was then continued until the temperature and percentage of material distilled showed that a portion of the added methyl behenate had passed into the distillate.

The methyl behenate was added to Sample 2 at the start of the distillation and the distillation was continued without interruption until a portion of the methyl behenate appeared in the distilled fractions. The curves in Fig. 1 are very similar and the difference in per cent distilled varied by only 0.3% in any one fraction. A small amount of C_{14} material appeared in the distillation

of Sample 2. This same material may have been present in Sample 1, but was not separated from the C_{16} fraction owing to less efficient use of the column.

Weighted totals of iodine values, refractive indices, naturally conjugated diene, and triene acids are given in Table I. No significant decreases in unsaturation are indicated from the data and the weighted total of refractive indices shows that no substantial amounts of esters with chain lengths greater than C_{22} were present in the safflower seed oil.

TABLE I

WEIGHTED TOTALS OF FRACTIONS COMPARED TO THE ORIGINAL ESTERS

	Sample 1		Sample 2	
	Esters	Total from fractions	Esters	Total from fractions
Iodine value	145.6	145.2	148.6	147.9
n_D^{55}	1.4460	1.4464	1.4466	1.4464
Naturally conjugated diene %	0.76	0.67	0.61	0.63
Naturally conjugated triene %	0.24	0.06	0.009	0.014

The analytical data on the distilled fractions for Samples 1 and 2 are presented in Tables II and III. The diene and triene acids in Fractions 8–13 in Table II and Fractions 8 and 9 in Table III were mainly naturally conjugated acids. The naturally conjugated acids appear in fractions toward the end of the distillation of the methyl esters of the oil and before the distillation of the methyl behenate. The effectiveness of the distillation column may be noted in the first fractions as shown by the abrupt change in saturated acid content.

TABLE II

ANALYTICAL VALUES FOR DISTILLED FRACTIONS FROM SAMPLE 1

Fraction	*B.p., °C.	Weight, %	Iodine value	n_D^{55}	Saponification value	Saturated, %	Monoene, %	Diene, %	Triene, %
1	185–205	5.2	4.8	1.4316	—	91.2	2.9	1.2	—
2	206	12.0	154.0	1.4463	—	9.1	2.3	83.9	—
3	206	12.4	160.7	1.4472	—	4.3	4.5	86.5	—
4	206	12.6	161.0	1.4472	—	3.7	5.4	86.2	—
5	206	12.6	159.7	1.4471	—	4.5	5.2	85.6	—
6	206	12.9	158.7	1.4468	—	4.1	7.1	84.1	—
7	206	12.4	156.6	1.4468	—	6.3	5.1	83.9	—
8	206	12.8	142.3	1.4456	191.6	6.8	19.6	68.9	0.03
9	206–212	1.2	110.6	1.4451	192.6	20.2	28.3	46.4	0.4
10	212–218	1.3	103.7	1.4462	192.1	30.5	18.5	42.8	3.5
11	218–245	1.6	79.5	1.4471	178.8	39.4	29.3	21.2	5.4
12	245–247	1.4	20.7	1.4395	161.0	75.4	17.6	1.6	0.7
13	248	0.2	7.9	1.4365	158.1	87.2	7.4	0.7	0.03
Unsaponifiable matter		1.4							

* *Boiling point at 10 mm. pressure.*

The data in Table III on Sample 2 are based on the sum total of the methyl esters of the safflower seed oil and the methyl behenate. The material in the still pot was assumed to have the same composition as the last fraction which was distilled. The relatively high content of unsaponifiable material in the still pot contributes to erroneous values for diene and triene acids, and a composition calculated on this basis is unreliable. This interference by unsaponifiable material has been reported by other research workers (7).

TABLE III

ANALYTICAL VALUES FOR DISTILLED FRACTIONS FROM SAMPLE 2

Fraction	B.p., °C.	Weight, %	Iodine value	n_D^{55}	Saponification value	Saturated, %	Monoene, %	Diene, %	Triene, %
1	169–187	0.4	17.5	1.4333	—	80.0	10.9	4.2	0.2
2	187–205	3.4	9.5	1.4290	—	89.3	2.3	3.7	—
3	206	16.8	161.0	1.4471	194.6	3.4	5.2	86.7	—
4	206	16.9	162.1	1.4475	192.7	3.6	4.4	87.3	—
5	206	16.3	160.6	1.4472	191.0	4.7	3.7	86.9	—
6	206	15.0	154.3	1.4466	192.0	4.3	11.5	79.5	—
7	206–210	3.4	123.6	1.4440	192.1	17.7	18.6	59.0	—
8	210–230	1.5	104.3	1.4486	190.1	26.9	20.0	47.7	0.7
9	230–248	1.0	65.8	1.4450	182.7	46.5	24.1	24.3	0.4
10	248	1.7	7.5	1.4374	165.6	87.4	7.3	0.5	—
11	248	22.6	2.7	1.4367	161.5	92.4	2.7	0.2	—
Unsaponifiable matter		1.0							

The data in Tables II and III were used to calculate the fatty acid composition presented in Table IV. Boiling point and saponification values were used to assign chain lengths to the various acids in a particular fraction. The methyl behenate which was added as a chaser was accounted for first in the calculation of fatty acid composition and the remaining acids were those originally present in the safflower seed oil. The dienoic and trienoic acids were assumed to belong

TABLE IV

FATTY ACID COMPOSITION OF SAFFLOWER SEED OIL

Fatty acid	Sample 1	Sample 2	Barker and Hilditch
Myrsitic	—	0.4	Trace
Palmitic	5.1	4.1	6.4
Stearic	6.5	5.4	3.1
Arachidic	0.5	1.0	0.2
Behenic	1.2	0.5	—
Hexadecenoic	0.1	0.2	—
Oleic	7.5	7.1	13.4
Eicosenoic	0.3	0.3	—
Erucic	0.2	0.9	—
Linoleic	78.5	80.0	76.9
Linolenic	0.1	0.1	—

to the C_{18} series irrespective of the fraction in which these occurred. The relatively large proportion of linoleic acid in the oil would make this acid the most likely to carry over into any other fraction and the triene acid appeared mainly as conjugated material.

The fatty acid compositions of the two samples show fair agreement. The second sample which had a higher iodine value would be expected to have a relatively higher content of unsaturated acids. The composition of safflower seed oil as determined by Barker and Hilditch (1) is included in Table IV for comparison. The most striking difference is shown in the relative proportions of oleic and saturated acids.

The values for saturated, oleic, linoleic, and linolenic acids for the oil, methyl esters, and total from the fractions are given in Table V. There are some differences between the analyses of the oil and esters and the total from the fractions. These are particularly noticeable in the content of saturated acids.

TABLE V

FATTY ACID COMPOSITION OF SAFFLOWER SEED OIL

Fatty acid	Sample 1			Sample 2		
	Oil	Esters	Total from fractions	Oil	Esters	Total from fractions
Saturated	11.1	11.4	13.2	9.4	10.0	11.4
Oleic	8.6	9.2	8.2	8.0	7.8	8.5
Linoleic	80.0	79.1	78.5	82.5	82.1	80.0
Linolenic	0.3	0.3	0.1	0.1	0.1	0.1

CONCLUSIONS

The removal of the unsaponifiable material from the safflower seed oil prior to the conversion of the glycerides to methyl esters apparently contributed to thermal destruction of the unsaturated acids. The nature of this destruction was not investigated further. However it would seem that the unsaponifiable fraction contains material which strongly inhibits such thermal destruction.

The use of methyl behenate as a "chaser" aided in the computation of the fatty acid composition since it facilitated a more complete distillation of the safflower oil esters than would otherwise have been possible owing to the holdup of the fractionation column. The fatty acid composition shows about the same level of linoleic acid as reported by other workers but the amounts of oleic and saturated acids are reversed. Linolenic acid is present in small amounts and the spectral analyses indicate it is mainly a naturally conjugated triene.

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